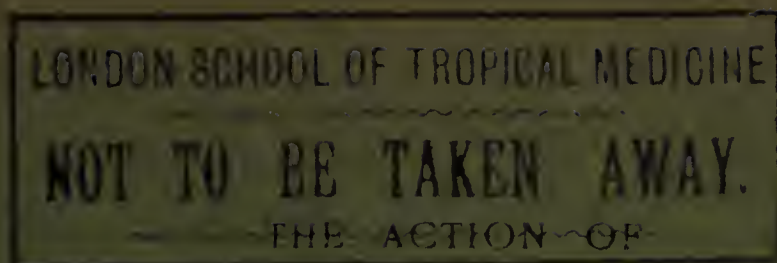


No. 14



14

THIONYL CHLORIDE

ON THE

METHYLENE ETHERS

OF

CATECHOL DERIVATIVES

PART II.

PIPERONYLOIN, PIPERIL AND HYDROPIPEROIN

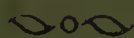
BY

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AND

ARTHUR JAMES EWINS, B.SC.

(From the "Transactions of the Chemical Society," 1908)



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LXVIII.—*The Action of Thionyl Chloride on the
Methylene Ethers of Catechol Derivatives. Part II.
Piperonyloin, Piperil, and Hydropiperoin.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

RECENTLY, one of us has shown (Trans., 1908, **93**, 563) that the methylene ethers of catechol derivatives are converted into the corresponding cyclic carbonates by heating with an excess of thionyl chloride

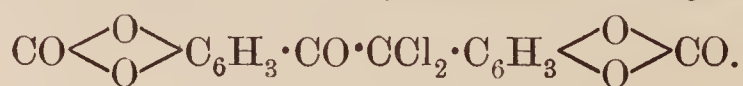
to 180—200°. The same carbonates are formed by treatment of the chlorine derivatives, which result from the action of phosphorus pentachloride on the methylene ethers, with cold water, so that the effect of thionyl chloride is equivalent to that of phosphorus pentachloride and water.

In the previous paper, the action of thionyl chloride on piperonyl alcohol, piperonal, and piperonylic acid was described; in the present one, we deal with its action on compounds containing two catechol nuclei, namely, piperonyloin, piperil, and hydro- and isohydro-piperoin. A large excess of thionyl chloride was found to be necessary, and serves as solvent from which the reaction product crystallises on cooling. With smaller quantities of thionyl chloride, whether in the presence or absence of an indifferent solvent, a great deal of decomposition always took place. Besides oxidising the methylene groups to carbonyl, thionyl chloride chlorinates the fatty chain linking the two benzene nuclei. The symmetrical grouping, $\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})$, of hydropiperoin is thus converted into $\text{CHCl}\cdot\text{CHCl}$, but the asymmetrical grouping of piperonyloin, $\text{CH}(\text{OH})\cdot\text{CO}$, is oxidised to $\text{CCl}_2\cdot\text{CO}$, so that the same substance is obtained as from the diketone piperil. Under the conditions employed in the production of cyclic carbonates, thionyl chloride was found to act in an analogous way on benzoin and benzil, oxidising the former, and converting both to dichlorobenzil, in the same way that phosphorus pentachloride acts on these substances.

Only in the case of the chloro-derivative from piperonyloin (and piperil) were we able to remove the chlorine from the fatty chain; we thus obtained a dicarbonate of tetrahydroxybenzil, and, from this, tetrahydroxybenzil itself; the constitution of the latter substance was proved by conversion into veratril, previously obtained from veratraldehyde.

EXPERIMENTAL.

3 : 4 : 3' : 4'-Dicarbonyldioxy- $\alpha\alpha$ -dichlorodeoxybenzoin,



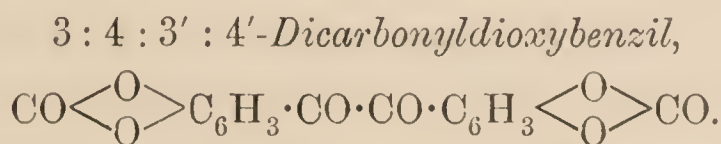
2.5 Grams of piperonyloin were heated with 10 c.c. of thionyl chloride in a sealed tube to 180° for seven hours. There was an unusually great pressure in the tube, and, on opening, sulphur dioxide and hydrogen chloride escaped. On cooling in a freezing mixture, the dark red solution deposited crystals, which were collected, washed with benzene, and recrystallised from xylene. Warty masses were obtained, which, after several crystallisations, separated in short, broad prisms melting at 191—192°. The yield was 60 per cent. of the theoretical:

0.1770 gave 0.3270 CO₂ and 0.0264 H₂O. C = 50.5 ; H = 1.7.

0.1421 „ (by fusion with potassium nitrate and sodium carbonate)
0.1094 AgCl. Cl = 19.0.

C₁₆H₆O₇Cl₂ requires C = 50.4 ; H = 1.6 ; Cl = 18.6 per cent.

The molecular weight was determined, by a microscopic method which we described some time ago (Trans., 1905, **87**, 1756), in glacial acetic acid at 85—90°, benzil being employed as standard. 0.157 Gram in 2.73 grams of acetic acid was intermediate between 0.16 mol. and 0.18 mol., whence M = 320—360, mean 340. C₁₆H₆O₇Cl₂ requires M = 381.

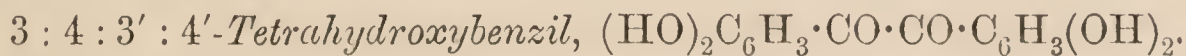


0.5 Gram of the substance just described was boiled with 10 c.c. of anhydrous formic acid ; hydrogen chloride was evolved, and the substance gradually passed into solution. When no more hydrogen chloride was given off, the hot solution was filtered. On cooling, long, thin prisms separated, melting at 214—215° with effervescence, characteristic of catechol carbonates. After washing with cold water, until the washings were not coloured by ferric chloride, in order to remove a little of the corresponding free catechol derivative, the crystals were dried over sulphuric acid in a vacuum and analysed ; the melting point remained unchanged :

0.0828 gave 0.1776 CO₂ and 0.0228 H₂O. C = 58.5 ; H = 2.9.

C₁₆H₆O₈ requires C = 58.9 ; H = 1.8 per cent.

3 : 4 : 3' : 4'-Dicarbonyldioxybenzil is readily hydrolysed by boiling with water, or by the addition of alkali, to tetrahydroxybenzil.



The removal of the two chlorine atoms from the product of the reaction between thionyl chloride and piperonyloin, without hydrolysing the carbonate, was accomplished by formic acid, as stated above, but the other reagents employed for a similar purpose by Pauly (*Ber.*, 1907, **40**, 3096), namely, oxalic acid, succinic acid, and sulphuric acid, were found to be unsuitable for this purpose, no pure carbonate being obtainable. The crude reaction product, however, readily yielded tetrahydroxybenzil on boiling with water. One gram of 3 : 4 : 3' : 4'-dicarbonyldioxy- α -dichlorodeoxybenzoin was intimately mixed with 0.3 gram of anhydrous oxalic acid, and the mixture was carefully heated until there was no longer any evolution of gas. It was then boiled with water for several hours, a little animal charcoal being added towards the end. On concentrating the filtered solution,

the substance crystallised; it was recrystallised from water and dried at 110° :

0.1588 gave 0.3573 CO_2 and 0.0510 H_2O . $\text{C} = 61.4$; $\text{H} = 3.6$.

$\text{C}_{14}\text{H}_{10}\text{O}_6$ requires $\text{C} = 61.3$; $\text{H} = 3.6$ per cent.

Tetrahydroxybenzil forms yellow prisms melting at 236° . It is readily soluble in hot water, from which it separates with two molecules of water of crystallisation:

0.4020, dried in desiccator until of constant weight, lost 0.0459 at 110° . $\text{H}_2\text{O} = 11.4$.

$\text{C}_{14}\text{H}_{10}\text{O}_6 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.6$ per cent.

Tetrahydroxybenzil is slightly soluble in cold water, readily so in alcohol, and dissolves in alkalis with an orange-red colour.

Tetrabenzoxxybenzil, $\text{C}_{14}\text{H}_6\text{O}_6(\text{CO} \cdot \text{C}_6\text{H}_5)_4$.

0.5 Gram of tetrahydroxybenzil was dissolved in 5 grams of pyridine, and 2 grams (eight molecular proportions) of benzoyl chloride were added. After standing for eighteen hours, the solution was poured into dilute sulphuric acid. The amorphous solid which separated was crystallised from benzene and afterwards from ethyl acetate, and then formed long, thin needles melting at 202° :

0.1573 gave 0.4182 CO_2 and 0.0501 H_2O . $\text{C} = 72.5$; $\text{H} = 3.5$.

$\text{C}_{42}\text{H}_{26}\text{O}_{10}$ requires $\text{C} = 73.0$; $\text{H} = 3.7$ per cent.

Constitution of Tetrahydroxybenzil.

The constitution assigned above to this substance follows, firstly, from its method of preparation; secondly, from its direct production from piperonyloin, and thirdly, from its conversion into tetramethoxybenzil or veratril. The substance is produced directly from piperonyloin by heating with 1—2 per cent. hydrochloric acid to 180° for several hours, but the yield is extremely small (less than 10 per cent.); its identity with the substance obtained by thionyl chloride resulted from the melting point of the mixture.

The conversion of tetrahydroxybenzil into its tetramethyl ether (veratril) was carried out by dissolving 0.5 gram in the minimum quantity of methyl alcohol, and adding 0.7 c.c. (four molecular proportions) of dimethyl sulphate and then four molecular proportions of an aqueous 40 per cent. potassium hydroxide solution. The same amounts of dimethyl sulphate and potassium hydroxide were added a second time. On dilution with water, a bright yellow solid separated, which was crystallised from a mixture of 3 parts of alcohol and 1 part of benzene, and formed yellow prisms melting at 220° . This substance was

There can scarcely be any doubt that this substance is 3:4:3':4'-dicarbonyldioxy- $\alpha\beta$ -dichloro-s-diphenylethane,



It melts at 260°, and is insoluble in water and sparingly soluble in most organic solvents; it dissolves in sodium carbonate or sodium hydroxide with an intense green colour. When the substance is boiled with water for some time, it yields a catechol derivative, as the solution gives a green coloration with ferric chloride. The catechol derivative is also formed by pyridine, and by benzylation of the crude product by Einhorn's method a crystalline substance, melting at 123—124°, was obtained, free from chlorine and from nitrogen, which probably represented a benzoyl derivative of the catechol substance. The yield was too small for analysis, and, as the original chlorocarbonate could only be isolated in small quantity and in some experiments not at all, further work had to be abandoned.

The action of thionyl chloride on hydropiperoin is somewhat complex; only in one experiment was the above chloro-compound (m. p. 260°) obtained at once in an approximately pure condition. Generally, at temperatures from 160° upwards, a mixture of two kinds of crystals was obtained. 2.5 Grams of hydropiperoin gave, for instance, 0.52 gram of small, grey needles melting at 230—235°, and 0.45 gram of larger, glassy crystals of a much higher melting point.

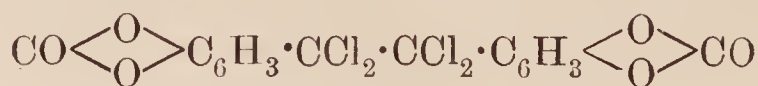
The former of these two substances could not be obtained pure, but the latter, which preponderated when hydropiperoin was heated with thionyl chloride to 220°, was obtained sufficiently pure to leave no doubt as to its composition. It was almost insoluble in most organic solvents, dissolved sparingly in boiling xylene, and was moderately soluble in boiling nitrobenzene, from which it was recrystallised several times. It formed stout prisms melting at 310—311° (silver nitrate bath):

0.1473 gave 0.2411 CO₂ and 0.0208 H₂O. C = 44.6; H = 1.6.

0.1018 „ 0.1326 AgCl. Cl = 32.3.

C₁₆H₆O₆Cl₄ requires Cl = 44.0; H = 1.4; Cl = 32.5 per cent.

The substance is derived from the chloro-compound melting at 260°, by the introduction of two more chlorine atoms, and is therefore 3:4:3':4'-dicarbonyldioxytetrachloro-s-diphenylethane; it is probably constituted according to one of the following formulæ:



(I.)



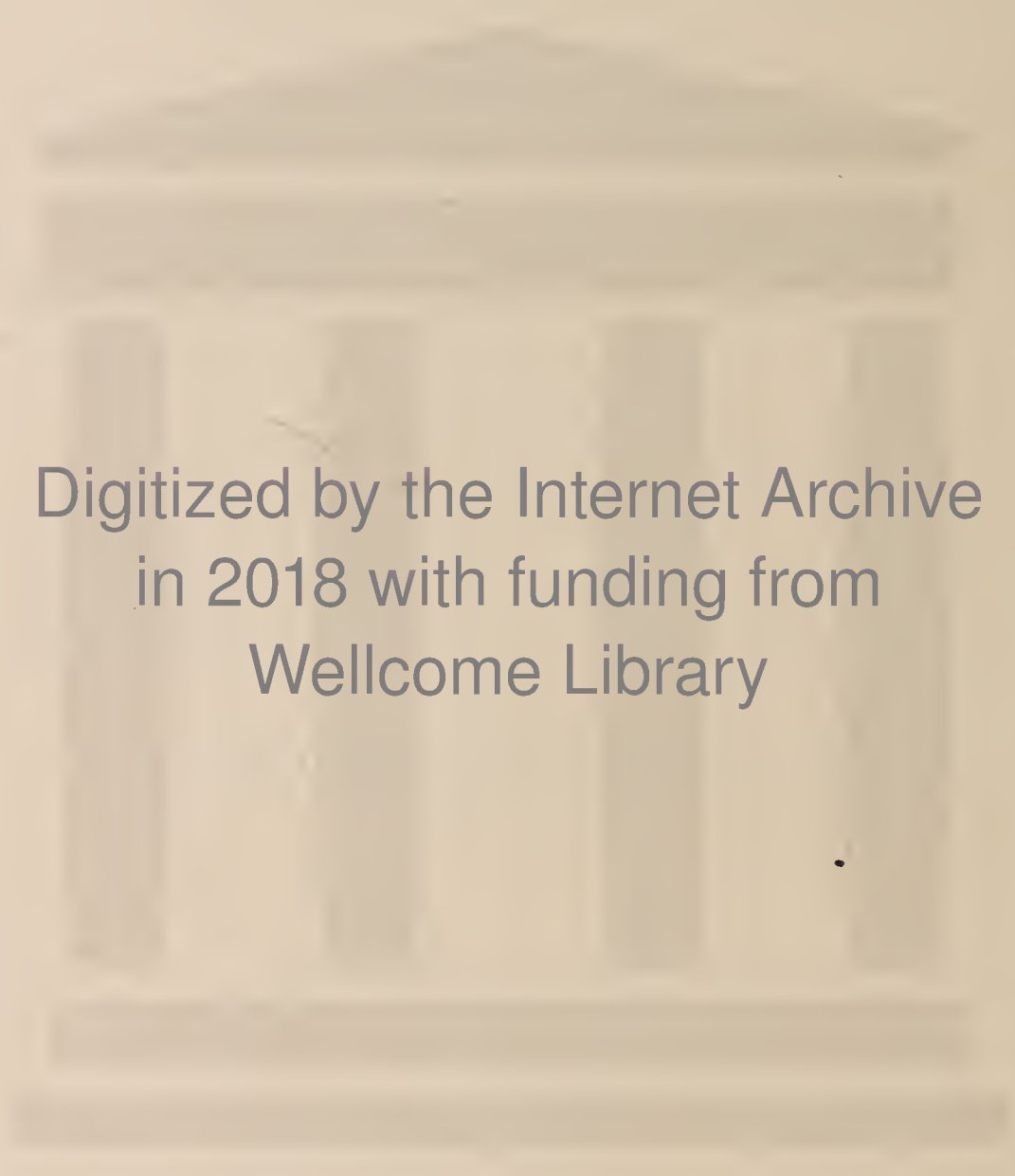
(II.)

The substance is extremely stable (except towards alkalis, which attack the carbonyl groups). Boiling for several hours with formic acid scarcely alters it; in this respect, it differs markedly from the similar dichloro-derivative obtained from piperonyloin. According to formula I, the substance would be a derivative of $\alpha\alpha\beta\beta$ -tetrachloro-*s*-diphenylethane, which is only attacked by glacial acetic acid at 200° ; this suggested the following experiment.

One gram of the substance, $C_{16}H_6O_6Cl_4$, was suspended in 10 c.c. of glacial acetic acid and heated to 200° for two hours. On cooling, 0.37 gram of the unchanged material was collected. The almost black filtrate gave an intense catechol reaction with ferric chloride; the acetic acid was therefore distilled off under diminished pressure, and the residue was boiled with water and animal charcoal. The almost colourless filtrate deposited in a vacuum over sulphuric acid a minute quantity of long needles, which decomposed at $290\text{--}300^{\circ}$ without melting. They were insoluble in cold water, but dissolved readily in alcohol; the alcoholic solution gave a green coloration with ferric chloride, changing to reddish-brown by a trace of alkali.

The fact that the whole of the chlorine was not removed, and that no tetrahydroxybenzil was obtainable, would indicate that some of the chlorine was in the benzene nuclei, and would therefore support formula II. The amount of substance available did not, however, allow us to investigate this point further.

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